Magnetically Hidden Order of Kramers Doublets in d^1 Systems: Sr_2VO_4

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We formulate and study an effective Hamiltonian for low-energy Kramers doublets of d^1-ions on a square lattice. We find that the system exhibits a magnetically hidden order in which the expectation values of the local spin and orbital moments both vanish. The order parameter responsible for a time-reversal symmetry breaking has a composite nature and is a spin-orbital analog of a magnetic octupole. We argue that such a hidden order is realized in the layered perovskite Sr_2VO_4.

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The ions with odd number of electrons have ground states which are at least doubly degenerate. The latter, known as Kramers degeneracy, is protected by time-reversal symmetry [1]. In Mott insulators the exchange interactions between Kramers doublets often induce a time-reversal symmetry breaking phase lifting the local degeneracy. As a result, a magnetic state with a well defined ordered pattern of local magnetic moments is formed at low temperatures, which, in turn, leads to the new Bragg peaks in neutron scattering experiments.

The above conventional picture may, however, fail for the insulating systems in which the local and non-local interactions between magnetically active degrees of freedom compete with each other. This competition may lead to a spontaneous time-reversal symmetry breaking through the development of a more complex order parameter, while the magnetic dipole moments of spin and orbital origin, being locally entangled, would remain disordered across the transition. The resulting order can be thus hidden to some experimental probes.

In this Letter we show that such a magnetically hidden order may be realized in transition-metal compounds. In the following we focus on a system of d^1 ions with partially filled t_{2g} levels on a square lattice, like the layered insulating compound Sr_2VO_4 [2, 3, 4]. Here, a square lattice of V^{4+} ions is formed in the ab-plane by corner-shared VO_6 octahedra, elongated along the c-axis. Sr_2VO_4 undergoes a phase transition on cooling at around $T_c \simeq 100$ K. The crystal structure remains tetragonal across the transition, the c/a ratio jumps to a somewhat higher value, and the magnetic susceptibility shows a sharp drop near T_c [4]. It has been suggested that a (weakly) first-order transition to an antiferromagnetic and orbitally ordered state could be responsible for the observed anomalies [4]. However, the neutron scattering experiments were not able to detect any magnetic order in the low temperature phase [2]. The nature of the ordered phase still remains experimentally unknown. Theoretically, as a possible candidate, a nontrivial orbital-stripe order coexisting with collinear antiferromagnetic spin order with large unit cell has been proposed [5].

Here, based on the microscopic theory, we propose that an unusual symmetry-breaking phase, induced by spin-orbit coupling and compatible with tetragonal crystal symmetry, is realized in Sr_2VO_4. We argue that the staggered ordering of composite spin-orbital objects, *magnetic octupoles*, is responsible for the phase transition. There is no static order of either spin or orbital magnetic moments in the ground state, hence the absence of magnetic Bragg peaks.

The octupolar order has thus far been discussed primarily in the context of f-electron systems [6, 7]. The peculiar physics of t_{2g} orbitals in tetragonal compounds uncovered here shows that this unusual state is well hosted by d-electron systems, too.

Low-energy effective Hamiltonian.– We first introduce the local degrees of freedom and then discuss the exchange interactions between them. The V^{4+} ion has a single unpaired electron residing in the t_{2g} manifold of xy, xz, and yz orbitals. The tetragonal elongation of the oxygen octahedra along the $z \parallel c$-axis only partly lifts the threefold orbital degeneracy: The xy orbital is pushed to a higher energy, while xz and yz orbitals remain degenerate. The orbital angular momentum is unquenched and the spin-orbit coupling is active. We thus start with a local Hamiltonian $H_0 = \Delta_{\rm cf}(\frac{2}{3} - l_z^2) - \lambda \vec{l}\cdot\vec{S}$ consisting of a tetragonal crystal field $\Delta_{\rm cf}$ and a spin-orbit coupling λ. Here $\vec{S}$ is an electron spin, and $l = 1$ is an effective angular momentum with $|l_z = 0\rangle \equiv |xy\rangle$, $|l_z = \pm 1\rangle \equiv -\frac{1}{\sqrt{2}}(i|xz\rangle \pm |yz\rangle)$. The total magnetic moment $\vec{M} = 2\vec{S} + \vec{L}$, where $\vec{L} = -\kappa\vec{l}$ is a true angular momentum and κ is a so-called covalency factor of order one [1]. The eigenstates of H_0 are spanned by three sets of Kramers doublets. The corresponding local level structure is schematically shown in Fig. 1(a). Concerning the energy scales involved, the *ab initio* study of Sr_2VO_4 electronic structure suggests $\Delta_{\rm cf} \simeq 80$ meV [5], and $\lambda \simeq 30$ meV for free V^{4+} ion is known experimentally [1]. In what follows, we retain only the two low-energy levels and neglect the one located at high energy $\sim \Delta_{\rm cf}$. We label Kramers partners within a doublet by isospin index $\tilde{\uparrow}$ and $\tilde{\downarrow}$ ($s^z = \pm\frac{1}{2}$), while the two doublets are denoted by pseudoorbital index $\pm$ ($\sigma^z = \pm 1$). The wave functions of the ground state doublet, $\sigma^z = +1$, are

$$|\tilde{\uparrow}\rangle_+ = |+1, \uparrow\rangle \ , \quad |\tilde{\downarrow}\rangle_+ = |-1, \downarrow\rangle \ . \tag{1}$$

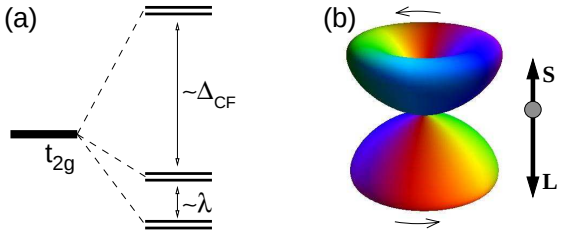

FIG. 1: (Color online) (a) A schematic view of the local level structure: the t_{2g} level is split into three sets of Kramers doublets by a tetragonal crystal field $\Delta_{\rm cf}$ and a spin-orbit coupling λ. (b) Density profile of an electron in the ground state doublet. The chirality of the isospin up wave function, associated with the gradient of its phase, is shown by small arrows. The electron spin $\vec{S}$ and orbital angular momentum $\vec{L}$ are coupled antiparallel to each other.

The corresponding electron density profile has an axial shape, and the two Kramers partners, apart from the direction of an electron spin, are distinguished by a chirality associated with the gradient of their phases determined by orbital angular momentum [see Fig. 1(b)].

The first excited level, located at an energy $\delta = \lambda + \frac{1}{4}(2\Delta_{\rm cf} - \lambda)(1/\cos 2\theta + 1)$, has the following eigenstates:

$$\begin{aligned} |\tilde{\uparrow}\rangle_- &= \sin\theta|-1,\uparrow\rangle + \cos\theta|0,\downarrow\rangle \ , \\ |\tilde{\downarrow}\rangle_- &= \sin\theta|+1,\downarrow\rangle + \cos\theta|0,\uparrow\rangle \ , \end{aligned} \qquad (2)$$

where $\tan 2\theta = 2\sqrt{2}\lambda/(\lambda - 2\Delta_{\rm cf})$. In the limit $\Delta_{\rm cf} \gg \lambda$ of interest here, $2\theta \sim \pi$ and $\delta \sim \lambda$.

We now discuss the interactions between neighboring ions. The effective Hamiltonian is obtained by projecting the corresponding t_{2g} superexchange model of Ref. [8] onto the reduced Hilbert space spanned by the two low energy Kramers doublets (1) and (2). We first consider the dominant part of the Hamiltonian and discuss later the effects of a finite Hund's coupling. We find

$$\mathcal{H} = J\sum_{\langle ij\rangle}(\vec{s}_i\cdot\vec{s}_j + \frac{1}{4})(1\pm\sigma_i^x)(1\pm\sigma_j^x) - \frac{\delta}{2}\sum_i \sigma_i^z \ , \quad (3)$$

where the first term describes the exchange coupling between the neighboring states, the $SU(2)$ isospin degrees of freedom are represented by $\vec{s}_i$, and Pauli matrices $\vec{\sigma}_i$ denote pseudo-orbitals, referred to as simply orbitals from now on (not to be confused with original t_{2g} orbitals). The upper (lower) sign is taken for a bond along $a(b)$ direction, $J = t^2/U$, where t is a transfer integral and U stands for the Coulomb repulsion. The local level splitting δ between two Kramers doublets is given by the second term.

The ground state properties.– The interaction between the isospins $\vec{s}_i$ in Eq. (3) depends on the orbital occupations through the operator $(1\pm\sigma_i^x)(1\pm\sigma_j^x)$. Since this operator is non-negative, the isospin exchange is purely antiferromagnetic (or equal to zero). This suggests that in the classical limit, $\langle\vec{s}_i\vec{s}_j\rangle = -\frac{1}{4}$, the expectation value of the first term in the Hamiltonian vanishes and all orbital configurations are degenerate. This extensive classical degeneracy, inherent to the coupled spin-orbital systems [8], is lifted here by the second term of the Hamiltonian [9] selecting uniform orbital order with $\sigma^z = +1$. The antiferromagnetic ordering of isospins $\vec{s}_i$ is then stabilized.

While the ground state in terms of staggered order of isospins may, at a first glance, look conventional, its physical properties are in fact very unusual and depend on the spatial orientation of the order parameter $\vec{m} \equiv \langle 2\vec{s}_{\mathbf{Q}}\rangle$ [$\mathbf{Q} = (\pi,\pi)$ is the ordering wave vector]. To illustrate this, we express the isospin $\vec{s}$ in terms of the original, physical spin $\vec{S}$ and angular momentum $\vec{l}$, operators:

$$s^{x(y)} = S^{x(y)}[(l^x)^2 - (l^y)^2] \ , \quad s^z = S^z \ . \qquad (4)$$

The in-plane components of isospins are represented by a composite object, which is, remarkably enough, a spin-orbital analog of a magnetic octupole. On the other hand, the axial component is equivalent to the physical spin. Thus, in-plane ordering of isospins ($\vec{m} \perp z$) corresponds to a staggered order of magnetic octupoles, while the axial one ($\vec{m} \parallel z$) corresponds to a magnetic dipolar order. In the former case, the local expectation values of both spin and angular moments are exactly zero: $\langle\vec{S}_i\rangle = \langle\vec{l}_i\rangle = 0$. This can be explicitly verified using the wave functions (1) of the ground state doublet: the in-plane g-factor of this doublet $g_{ab} \equiv 0$. In the case of a dipolar order, $\vec{m} \parallel z$, we find again a somewhat unusual picture: the value of ordered magnetic moments is strongly suppressed, $\langle M^z\rangle = 1 - \kappa \ll 1$, because of compensation between spin and orbital magnetic moments. In the absence of covalency, i.e. $\kappa = 1$, both $\langle M\rangle$ and $g_c = 2(1-\kappa)$ vanish.

The effective Hamiltonian (3), with isospin rotational symmetry, cannot select a direction of the order parameter $\vec{m}$: The latter can be rotated from a purely dipolar character to a purely octupolar one at no energy cost. In other words, a Goldstone mode describing the out-of-plane rotation of isospins corresponds physically to fluctuations between dipolar and octupolar orderings. However, the $SU(2)$ isospin symmetry is only approximate and is broken by Hund's coupling J_H, neglected so far. Finite J_H induces the anisotropy term, which in the present case is of easy-plane form $\mathcal{H}_\alpha(i,j) = -\alpha J s_i^z s_j^z$, with $\alpha = 2J_H/U \ll 1$. It confines the isospins in the plane and selects the staggered octupolar order, with vanishing dipolar moments $\langle\vec{S}_i\rangle$ and $\langle\vec{L}_i\rangle$ on every site. The emergence of this highly unusual state in an apparently simple d^1 Mott insulator like Sr_2VO_4 is surprising, given that its single-hole counterpart, d^9 perovskite La_2CuO_4, is a conventional antiferromagnet. The origin of new physics here is due to an unquenched spin-orbit coupling, the significance of which is being recognized in the context of various phenomena [10, 11, 12, 13, 14].

Excitation spectra.– We now turn to the excitation spectrum above the octupolar ordered state. We first study the Hamiltonian (3) at a mean-field level, decouple it into isospin and orbital sectors, and discuss later the interactions between them. We employ isospin (orbital) wave representation for $\vec{s}_i$ ($\vec{\sigma}_i$) operators in terms of Holstein-Primakoff bosons b_i (a_i) and diagonalize the harmonic part of the mean-field Hamiltonian.

The isospin (intradoublet) and orbital (interdoublet) excitation energies are given by $\omega_{\mathbf{k}} = 2J_s\sqrt{(1-\gamma_{\mathbf{k}}+\alpha\gamma_{\mathbf{k}})(1+\gamma_{\mathbf{k}})}$ and $\Omega_{\mathbf{k}} = \sqrt{\delta(\delta+8J_o\gamma_{\mathbf{k}})}$, respectively. Here $\gamma_{\mathbf{k}} = \frac{1}{2}(\cos k_x + \cos k_y)$, $J_s = J\langle 1+\sigma_i^x\sigma_j^x\rangle$, and $J_o = J\langle \vec{s}_i\vec{s}_j + \frac{1}{4}\rangle$. At $T=0$, we estimate $J_s \simeq J$ and $J_o \simeq -0.08J$. The dispersion relations are plotted in Fig. 2 (left) for the realistic values of the parameters ($\delta = 2.2$ and $\alpha = 0.2$ in units of J). The in-plane isospin excitations are gapless, while the out-of-plane gap ($\sim\sqrt{\alpha}$) at Γ point is induced by easy-plane anisotropy protecting octupolar order. The weakly dispersive interdoublet excitations are centered around δ.

The above elementary excitations correspond, in fact, to the fluctuations of rather unconventional degrees of freedom. The in-plane isospin waves represent octupolar excitations, not directly coupled to the conventional spectroscopic probes such as neutrons. To make some predictions for inelastic neutron scattering experiments, we now discuss the magnetic excitations. To this end, we express the local magnetic moment $\vec{M}_i$ in terms of isospin and orbital wave operators (b_i and a_i, respectively):

$$M_i^x \simeq (b_i + b_i^\dagger)(a_i + a_i^\dagger)\ , \quad M_i^y \simeq e^{\imath\mathbf{QR}_i}(a_i + a_i^\dagger)\ ,$$
$$M_i^z \simeq \imath(1-\kappa)e^{\imath\mathbf{QR}_i}(b_i - b_i^\dagger)\ . \qquad (5)$$

Here, only the leading order terms in boson operators are kept, and the isospin order parameter along y-axis is assumed. All three components of $\vec{M}_i$ consist of fluctuating parts only. Hence, no magnetic Bragg peaks will be seen in elastic scattering. The inelastic response of the ordered state is rather nontrivial. The fluctuations of M^y component, which have the largest spectral weight of order one, are given by orbital excitations only. We thus predict well-defined interdoublet excitations at energies $\sim\delta$ [upper curve in Fig. 2 (left)] to be observed by polarized neutrons. The out-of-plane magnetic response, M^z component in Eq. (5), corresponds to gapped out-of-plane isospin excitations. However, the small spectral weight $\sim(1-\kappa)^2$ would probably make it hard to detect them. The in-plane M^x response is given by the composite isospin-orbital excitations [see Eq. (5)]. The conventional spin wave excitations, inherent to magnetically ordered systems, are replaced here by a two-particle continuum [the shaded area in Fig. 2 (right)]. The latter is bounded from below by $\Omega_{\mathbf{k}+\mathbf{Q}}$, the interdoublet excitation energy at momentum shifted by $\mathbf{Q}$.

The interaction between isospin and orbital waves, neglected so far, dynamically induce a linear coupling between in-plane magnetic and isospin excitations. The three particle processes, responsible for this dynamic hybridization, have the following form (in units of J):

$$\mathcal{H}' = \sum_{\mathbf{k},\mathbf{q}}\{\eta_{\mathbf{p}}b_{\mathbf{q}}^\dagger b_{\mathbf{k}} + \eta_{\mathbf{k}}(b_{-\mathbf{k}}^\dagger b_{\mathbf{q}}^\dagger + b_{\mathbf{k}}b_{-\mathbf{q}})\}(a_{\mathbf{p}} + a_{-\mathbf{p}}^\dagger)\ , \quad (6)$$

where the matrix element $\eta_{\mathbf{p}} = (\cos p_x - \cos p_y)$, and $\mathbf{p} = \mathbf{q} - \mathbf{k}$. The second order perturbative correction from $\mathcal{H}'$ to the in-plane magnetic susceptibility χ_{xx} is given by the lower diagram in Fig. 2 (right). When this correction is included, the spectral function of in-plane magnetic excitations χ''_{xx} receives also a quasiparticle contribution. It lies below the continuum and is given by

$$\chi''_{xx}(\mathbf{k},\omega) = \left(\frac{J\eta_{\mathbf{k}}}{\delta+2J}\right)^2\sqrt{\frac{1-\gamma_{\mathbf{k}}}{1+\gamma_{\mathbf{k}}}}\ \delta(\omega-\omega_{\mathbf{k}})\ . \qquad (7)$$

Its intensity is peaked at X-point and dies out when approaching to the ordering wave vector [see Fig. 2 (right)]. The Goldstone mode is thus invisible, reflecting the absence of magnetic Bragg peaks. Along $(1,1)$ direction, the hybridization matrix element vanishes and the quasiparticle peak is absent.

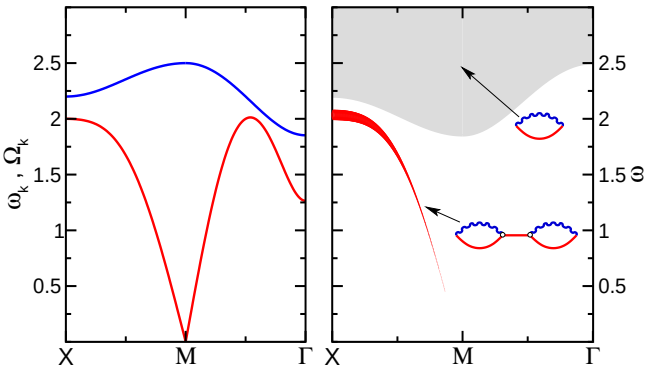

FIG. 2: (Color online) Left: The dispersions of elementary excitations along the direction $X(\pi,0) \to M(\pi,\pi) \to \Gamma$ in the Brillouin zone. The lower (upper) curve corresponds to the isospin (orbital) waves. Right: The spectrum of in-plane, M^x component, magnetic excitations. It consists of a continuum of composite, isospin-orbital excitations (shaded area), and a quasiparticle part (lower curve, the width scales with intensity). The corresponding diagrams are also shown: The solid (wavy) lines denote the isospin (orbital) excitations and the open dots stand for the three-particle vertex in Eq. (6). Energies are given in units of J.

Finite temperature transition.– We now turn to finite temperatures and show that interplay between interdoublet and intradoublet excitations leads to a first order phase transition. The in-plane ordering of isospins breaks their rotational symmetry around z-axis. Note that the uniform order of low-energy doublets, $\sigma \equiv \langle\sigma_i^z\rangle = +1$, conserves the tetragonal crystal symmetry, as xz and yz orbitals are equally occupied on every site. The scale of

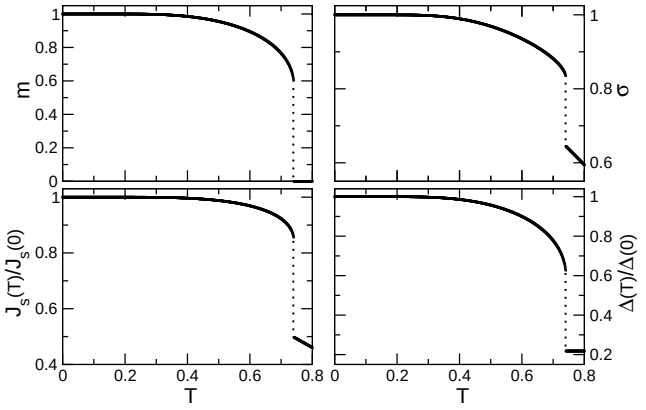

FIG. 3: The isospin m and orbital σ order parameters, isospin exchange J_s, and orbital gap Δ vs temperature. The broken lines mark corresponding jumps at the first order transition.

the transition temperature is set by the isospin exchange energy J_s, which depends on orbital correlations. On the other hand, the orbital correlations themselves are determined by isospin ones controlling the orbital exchange J_o. The nonlinear feedback effects between two degrees of freedom can drive a first order transition.

To substantiate the above picture, we employ a mean-field approach. The isospin order parameter m is given by a self-consistent equation $m = \tanh(mJ_s/T)$ with $J_s = J\langle 1 + \sigma_i^x\sigma_j^x\rangle$, where the orbital correlation function $\langle\sigma_i^x\sigma_j^x\rangle = \sum_{\mathbf{k}}\gamma_{\mathbf{k}}\delta/[\Omega_{\mathbf{k}}\tanh(\Omega_{\mathbf{k}}/2T)]$. The energy of orbital excitations $\Omega_{\mathbf{k}}$ is controlled by orbital exchange $J_o = J(1-m^2)/4$.

Shown in Fig. 3 are the temperature dependences of isospin and orbital order parameters, together with isospin exchange and orbital excitation gap Δ. The first order jumps are clearly seen in all physical quantities. This is compatible with the abrupt changes in lattice parameters and magnetic susceptibility observed experimentally near $T_c \simeq 100$ K [4, 15].

Fig. 3 shows that not only isospin order parameter m but also the exchange energy J_s jumps at the transition. This suggests pronounced magnetoelastic effects and explains an abrupt in-plane contraction of the crystal, enhancement of a c/a ratio. Note also that jumps in σ and Δ imply an increase of the population of the low-energy doublet. As the latter does not include planar xy orbital, Jahn-Teller coupling acts in the same direction as magnetoelastic effect and further enhances a c/a ratio. Finally, since the ground state doublet (1) is non-magnetic, the magnetic susceptibility drops at the transition to the level determined by the Van Vleck contribution from the transitions to the high energy doublets [16].

In conclusion, a magnetically hidden octupolar order may be induced by spin-orbit coupling in d^1 transition metal oxides. We have argued that such a hidden order is realized in the perovskite Sr_2VO_4, explaining thereby the puzzling absence of magnetic Bragg peaks in this Mott insulator. The present theory suggests a nontrivial magnetic excitation spectrum in the ordered state, that can be verified by neutron scattering experiments. The spin-resolved circularly polarized photoemission experiment would be another test of the present scenario. This technique measures the $\vec{l}\cdot\vec{S}$ scalar product [17], which we predict to be ~ 0.5 in the ground state. Finally, we suggest that another candidate to exhibit octupolar order is Sr_2NbO_4, in which a more pronounced spin-orbit coupling is expected. Sr_2NbO_4 is known to be a Mott insulator [18], however, its low temperature magnetic properties have not yet been reported.

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[1] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).
[2] M. Cyrot *et al.*, J. Solid State Chem. **85**, 321 (1990).
[3] J. Matsuno *et al.*, Phys. Rev. Lett. **95**, 176404 (2005).
[4] H.D. Zhou *et al.*, Phys. Rev. Lett. **99**, 136403 (2007).
[5] Y. Imai, I. Solovyev, and M. Imada, Phys. Rev. Lett. **95**, 176405 (2005).
[6] See, e.g., Y. Kuramoto, Prog. Theor. Phys. Suppl. **176**, 77 (2008), and references therein.
[7] A few exceptions include the case of frustrated magnets [T. Momoi, P. Sindzingre, and N. Shannon, Phys. Rev. Lett. **97**, 257204 (2006); M.E. Zhitomirsky, Phys. Rev. B **78**, 094423 (2008)], and possible order of complex e_g orbitals in ferromagnetic manganites [J. van den Brink and D. Khomskii, Phys. Rev. B **63**, 140416(R) (2001)].
[8] G. Khaliullin, Prog. Theor. Phys. Suppl. **160**, 155 (2005).
[9] At vanishing spin-orbit coupling, $\delta = 0$ and the quantum effects select the spin-singlet dimer states, see G. Jackeli and D.A. Ivanov, Phys. Rev. B **76**, 132407 (2007).
[10] O. Tchernyshyov, Phys. Rev. Lett. **93**, 157206 (2004).
[11] S. Gangadharaiah, J. Sun, and O.A. Starykh, Phys. Rev. Lett. **100**, 156402 (2008).
[12] G. Jackeli and G. Khaliullin, Phys. Rev. Lett. **102**, 017205 (2009).
[13] G. Chen, L. Balents, and A.P. Schnyder, Phys. Rev. Lett. **102**, 096406 (2009).
[14] A. Shitade *et al.*, Phys. Rev. Lett. **102**, 256403 (2009).
[15] Our mean-field study gives a transition temperature $T_{MF} \sim 0.74J$. Using $t = 0.19$ eV and $U = 2.58$ eV, suggested by *ab initio* calculations [5], we estimate $J \simeq 14$ meV, and find a reasonable value $T_{MF} \sim 120$ K.
[16] The susceptibility upturn seen at low temperatures is possibly due to spin-one V^{3+} impurities induced by the oxygen deficiency, see N. Suzuki, T. Noritake, and T. Hioki, Mater. Res. Bull. **27**, 1171 (1992).
[17] T. Mizokawa *et al.*, Phys. Rev. Lett. **87**, 077202 (2001); G. Ghiringhelli *et al.*, Phys. Rev. B **66**, 075101 (2002).
[18] K. Isawa and M. Nagano, Physica C **357-360**, 359 (2001).